

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

JMYT-239US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

To Be Assigned

057759

INTERNATIONAL APPLICATION NO.

PCT/GB99/04081

INTERNATIONAL FILING DATE

09 December 1999 (09.12.99)

PRIORITY DATE CLAIMED

09 December 1998 (09.12.98)

TITLE OF INVENTION

ELECTRODE STRUCTURE

APPLICANT(S) FOR DO/EO/US

COOPER, Susan Joy

HOOGERS, Gregor

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- ☒ A copy of the International Search Report (PCT/ISA/210).
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (UNEXECUTED)
- ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
- ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

To Be Assigned

PCT/GB99/04081

JMYT-239US

21. The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :**

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$970.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$840.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$690.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$670.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$96.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	17 - 20 =	0	x \$18.00	\$0.00
Independent claims	2 - 3 =	0	x \$80.00	\$0.00

Multiple Dependent Claims (check if applicable). ☐

\$0.00

**TOTAL OF ABOVE CALCULATIONS =**

\$860.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐

\$0.00

**SUBTOTAL =**

\$860.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

\$0.00

**TOTAL NATIONAL FEE =**

\$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐

\$0.00

**TOTAL FEES ENCLOSED =**

\$860.00

Amount to be:  
refunded \$  
charged \$

☒ A check in the amount of \$860.00 to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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SIGNATURE

Christopher R. Lewis

NAME

36,201

REGISTRATION NUMBER

June 8, 2001

DATE

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Susan Joy Cooper et al. : Art Unit:  
Application No.: To Be Assigned : Examiner:  
Filed: Herewith :  
FOR: ELECTRODE STRUCTURE :

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

**IN THE SPECIFICATION:**

Please replace the paragraph beginning at page 13, line 5, with the following:

In a future aspect, the present invention provides a fuel cell comprising an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M where M is a metal alloyed with the platinum.

**IN THE CLAIMS:**

Please replace claims 1-3 and 5-11 with the following amended claims:

1. (Amended) An electrode structure comprising a first catalytic component and a second catalytic component, wherein:

- 3 (a) said first catalytic component comprises one or more  
4 electrocatalyst(s) of formula Pt-Y, wherein Y is Mo, W or an  
5 oxide of Mo or W; and
- 6 (b) said second catalytic component comprises one or more  
7 electrocatalyst(s) of formula Pt-M, where M is a metal alloyed  
8 with the platinum and is one or more metals selected from the  
9 group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn;  
10 and

11 wherein the first and second catalytic components are in ionic contact with  
12 each other.

1 2. (Amended) An electrode structure according to claim 12  
2 wherein X is selected from Ru, Mn, Co, Ni, and Rh.

1 3. (Amended) An electrode structure according to claim 1,  
2 wherein M is selected from Ru or Rh.

1 5. (Amended) An electrode comprising an electrode structure  
2 according to claim 1 wherein the electrocatalyst materials are present on one  
3 side of a gas diffusion material.

1 6. (Amended) A catalysed membrane comprising an electrode  
2 structure according to claim 1 wherein the electrocatalyst materials are  
3 present on one side of a polymer electrolyte membrane material.

1 7. (Amended) An MEA comprising an electrode structure  
2 according to claim 1.

1 8. (Amended) An electrode according to claim 5, wherein the two  
2 catalyst materials are formulated into two separate layers.

1 9. (Amended) An electrode according to claim 5, wherein the two  
2 catalyst materials are formulated into one mixed layer.

1           10     (Amended) A fuel cell comprising an electrode structure,  
2     comprising a first catalytic component and a second catalytic component,  
3     characterised in that the first catalytic component comprises one or more  
4     electrocatalyst(s) of formula Pt-Y where Y is Mo, W, or an oxide of Mo or  
5     W, and the second catalytic component comprises one or more  
6     electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the  
7     platinum and is one or more metals selected from the group Ru, Rh, Ti, Cr,  
8     Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn, and wherein the first and second  
9     catalytic components are in ionic contact with each other.

1           11.    (Amended) Use of an electrode structure according to claim 1  
2     in a fuel cell.

Please add the following new claims:

1           12.    (Newly Added) An electrode structure according to claim 1  
2     wherein said first catalytic component comprises a third metal component X  
3     which is alloyed with the platinum and which is one or more metals selected  
4     from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn.

1           13.    (Newly Added) A catalysed membrane according to claim 6  
2     wherein the two catalyst materials are formulated into two separate layers.

1           14.    (Newly Added) A catalysed membrane according to claim 6  
2     wherein the two catalyst materials are formulated into one mixed layer.

1           15.    (Newly Added) An MEA according to claim 7 wherein the two  
2     catalyst materials are formulated into two separate layers.

Please cancel claim 16.

1           17.    (Newly Added) An MEA according to claim 7 wherein the two  
2     catalyst materials are formulated into one mixed layer.

1           18.    (Newly Added) A fuel cell according to claim 10 wherein said  
2     first catalytic component comprises a third metal component X which is

- 3 alloyed with the platinum and which is one or more metals selected from the  
4 group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn.

IN THE ABSTRACT:

Please replace the abstract with the new abstract which is attached as a separate sheet.

Respectfully submitted,



Christopher R. Lewis, Reg. No. 36,201  
Attorney for Applicants

CRL/lrb

Enclosures: Amended Abstract  
Version with markings to show changes made

Dated: June 8, 2001

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The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.

EXPRESS MAIL Mailing Label No.: **EL854574786US**  
Date of Deposit: **June 8, 2001**

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10 and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

  
Kathleen Libby

ABSTRACT

A poison tolerant anode structure for use in fuel cells, in particular suitable for use on proton exchange membrane fuel cells, comprising a first catalytic component Pt-Y where Y is a bronze forming element, and optionally a third metal X alloyed with the platinum, and a second catalytic component Pt-M where M, metal, is alloyed with the platinum. An anode, a catalysed membrane, a membrane electrode assembly and a fuel cell comprising the electrode structure, are disclosed.

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION:**

Specification at page 13, line 5:

In a future aspect, the present invention provides a fuel cell comprising an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M where M is a metal alloyed with the platinum.

**IN THE CLAIMS:**

1. (Amended) An electrode structure comprising a first catalytic component and a second catalytic component, wherein:

(a) said first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y, wherein Y is Mo, W or an oxide of Mo or W, and optionally a third metal component X which is alloyed with the platinum and which is one or metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; and

(b) said second catalytic component comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum and is one or more metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; and

wherein the first and second catalytic components are in ionic contact with each other.

2. (Amended) An electrode structure according to claim 1 wherein X is selected from Ru, Mn, Co, Ni, and Rh and Ni.



1           3. (Amended) An electrode structure according to claim 1 ~~or~~  
2 ~~claim 2~~, wherein M is selected from Ru or Rh.

1           5. (Amended) An electrode comprising an electrode structure  
2 according to ~~any preceding claim 1~~ wherein the electrocatalyst materials are  
3 present on one side of a gas diffusion material.

1           6. (Amended) A catalysed membrane comprising an electrode  
2 structure according to ~~any one or more of claims 1 to 4~~ claim 1 wherein the  
3 electrocatalyst materials are present on one side of ~~the~~ a polymer electrolyte  
4 membrane material.

1           7. (Amended) An MEA comprising an electrode structure  
2 according to ~~any one or more of claims 1 to 4~~ claim 1.

1           8. (Amended) An electrode according to claim 5, ~~a catalysed~~  
2 ~~membrane according to claim 6 or an MEA according to claim 7~~ wherein the  
3 two catalyst materials are formulated into two separate layers.

1           9. (Amended) An electrode according to claim 5, ~~a catalysed~~  
2 ~~membrane according to claim 6 or an MEA according to claim 7~~ wherein the  
3 two catalyst materials are formulated into one mixed layer.

1           10 (Amended) A fuel cell comprising an electrode structure,  
2 comprising a first catalytic component and a second catalytic component,  
3 characterised in that the first catalytic component comprises one or more  
4 electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and  
5 optionally a third metal component X which is alloyed with the platinum Mo,  
6 W, or an oxide of Mo or W, and the second catalytic component ~~which~~  
7 comprises one or more electrocatalyst(s) of formula Pt-M, where M is a  
8 metal alloyed with platinum and is one or more metals selected from the  
9 group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn, and wherein  
10 the first and second catalytic components are in ionic contact with each other.

1           11. (Amended) Use of an electrode structure according to ~~any one~~  
2 ~~or more of claims 1 to 8~~ claim 1 in a fuel cell.

Claims 12-15 have been added.

Claim 16 has been canceled.

Claims 17 and 18 have been added.

IN THE ABSTRACT:

A ~~piston~~ poison tolerant anode structure for use in fuel cells, in particular suitable for use on proton exchange membrane fuel cells, comprising a first catalytic component Pt-Y where Y is a bronze forming element, and optionally a third metal-~~X~~ X alloyed with the platinum, and a second catalytic component ~~It-M~~ Pt-M where M, metal, is alloyed with the platinum. An anode, a catalysed membrane, a membrane electrode assembly and a fuel cell comprising ~~said~~ the electrode structure, are disclosed.

ELECTRODE STRUCTURE

The invention relates to an improved electrode structure and specifically to a poison-tolerant anode structure for fuel cells, suitable for use in particular in proton exchange membrane fuel cells. The invention further relates to an anode, a catalysed membrane, a  
5 membrane electrode assembly and a fuel cell comprising said electrode structure.

Electrochemical cells invariably comprise at their fundamental level a solid or liquid electrolyte and two electrodes, the anode and cathode, at which the desired electrochemical reactions take place. A fuel cell is an energy conversion device that  
10 efficiently converts the stored energy of its fuel into electrical energy by combining hydrogen, stored as a gas, or methanol, stored as a liquid or gas, with oxygen to generate electrical power. The hydrogen or methanol is oxidised at the anode and oxygen reduced at the cathode. In these cells gaseous reactants and/or products have to be diffused into and/or out of the cell electrode structures. The electrodes therefore are  
15 specifically designed to be porous to gas diffusion in order to optimise the contact between the reactants and the reaction sites in the electrode to maximise the reaction rate. An electrolyte is required which is in contact with both electrodes and which may be alkaline or acidic, liquid or solid. In a solid polymer fuel cell (SPFC), also known as a proton-exchange membrane fuel cell (PEMFC), the electrolyte is a solid proton-conducting polymer membrane, commonly based on perfluorosulphonic acid materials.  
20 These electrolytes must be maintained in a hydrated form during operation in order to prevent loss of ionic conduction through the electrolyte; this limits the operating temperature of the PEMFC to between 70°C and 120°C, depending on the operating pressure. The PEMFC does, however, provide much higher power density output than

the other fuel cell types, and can operate efficiently at much lower temperatures. Because of this, it is envisaged that the PEMFC will find use in vehicular power generation and small-scale residential power generation applications. In particular, vehicle zero-emission regulations have been passed in areas of the United States that are likely to restrict the use of the combustion engine in the future. Pre-commercial PEMFC-powered buses and prototype PEMFC-powered vehicles are now being demonstrated for these applications.

Due to the relatively low operating temperatures of these systems, the oxidation and reduction reactions require the use of catalysts in order to proceed at useful rates. Catalysts, which promote the rates of electrochemical reactions, such as oxygen reduction and hydrogen oxidation in a fuel cell, are often referred to as electrocatalysts. Precious metals, in particular platinum, have been found to be the most efficient and stable electrocatalysts for all low-temperature fuel cells operating below 300°C. The platinum electrocatalyst is provided as very small particles (~20-50Å) of high surface area, which are often, but not always, distributed on and supported by larger macroscopic conducting carbon particles to provide a desired catalyst loading. Conducting carbons are the preferred materials to support the catalyst.

In the PEMFC the combined laminate unit formed from the membrane and the two electrodes is known as a membrane electrode assembly (MEA). The MEA will typically comprise several layers, but can in general be considered, at its basic level, to have five layers, which are defined principally by their function. On either side of the membrane an anode and cathode electrocatalyst is incorporated to increase the rates of

the desired electrode reactions. In contact with the electrocatalyst containing layers, on the opposite face to that in contact with the membrane, are the anode and cathode gas diffusion substrate layers. The anode gas diffusion substrate is designed to be porous and to allow the reactant hydrogen or methanol to enter from the face of the substrate exposed to the reactant fuel supply, and then to diffuse through the thickness of the substrate to the layer which contains the electrocatalyst, usually platinum metal based, to maximise the electrochemical oxidation of hydrogen or methanol. The anode electrocatalyst layer is also designed to comprise some level of the proton conducting electrolyte in contact with the same electrocatalyst reaction sites. With acidic electrolyte types the product of the anode reaction are protons and these can then be efficiently transported from the anode reaction sites through the electrolyte to the cathode layers. The cathode is also designed to be porous and to allow oxygen or air to enter the substrate and diffuse through to the electrocatalyst layer reaction sites. The cathode electrocatalyst combines the protons with oxygen to produce water. Product water then has to diffuse out of the cathode structure. The structure of the cathode has to be designed such that it enables the efficient removal of the product water. If water builds up in the cathode, it becomes more difficult for the reactant oxygen to diffuse to the reaction sites, and thus the performance of the fuel cell decreases. In the case of methanol fuelled PEMFCs, additional water is present due to the water contained in the methanol, which can be transported through the membrane from the anode to the cathode side. The increased quantity of water at the cathode requires removal. However, it is also the case with proton exchange membrane electrolytes, that if too much water is removed from the cathode structure, the membrane can dry out and the performance of the fuel cell also decreases.

The complete MEA can be constructed by several methods. The electrocatalyst layers can be bonded to one surface of the gas diffusion substrates to form what is known as a gas diffusion electrode, which can be either an anode or a cathode. The MEA is then formed by combining two gas diffusion electrodes with the solid proton-conducting membrane. Alternatively, the MEA may be formed from two porous gas diffusion substrates and a solid proton-conducting polymer membrane which has been catalysed on both sides; or indeed the MEA may be formed from one gas diffusion electrode and one gas diffusion substrate and a solid proton-conducting polymer catalysed on the side facing the gas diffusion substrate.

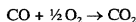
Electrodes, catalysed membranes or MEA's are employed in many different electrochemical devices in addition to fuel cells, including metal-air batteries, electrochemical gas sensors, and electrochemical reactors for the electrosynthesis of useful chemical compounds.

In most practical fuel cell systems, the hydrogen fuel is produced by converting a hydrocarbon-based fuel (such as methane) or an oxygenated hydrocarbon fuel (such as methanol) to hydrogen in a process known as reforming. This fuel, referred to as reformat, contains (in addition to hydrogen) high levels of carbon dioxide ( $\text{CO}_2$ ), of around 25%, and small amounts of impurities such as carbon monoxide (CO), typically at levels of around 1%. For fuel cells operating at temperatures below  $200^\circ\text{C}$ , and especially for the PEMFC operating at temperatures around  $100^\circ\text{C}$ , it is well known that CO, even at levels of 1-10ppm, is a severe poison for the platinum electrocatalysts

present in the electrodes. This leads to a significant reduction in fuel cell performance, ie the cell voltage at a given current density is reduced. This deleterious effect is more pronounced in PEMFCs operating at lower temperatures. In addition, it has been found that the CO<sub>2</sub> present in the fuel stream can also cause a loss of performance. This performance decay is usually small compared to the effect of CO.

Various methods have been employed to alleviate anode CO poisoning. For example, reformer technology has been redesigned to include an additional catalytic reactor, known as a preferential or selective oxidation reactor. This involves the injection of air or oxygen into the hydrogen-containing reactant gas stream, prior to it passing over the selective oxidation catalyst, to oxidise the CO to CO<sub>2</sub>. This can reduce the levels of CO from 1-2% down to below 100ppm. However, even at these levels, the anode electrocatalyst in the PEMFC is still poisoned.

It has also been found that poisoning of the electrocatalyst by CO at levels of 1-100ppm can be reduced by the use of an oxygen or air bleed directly into the anode gas stream just before it enters the anode chamber of the fuel cell itself. This is described by Gottesfeld and Pafford in J. Electrochem. Soc., 135, 2651 *et seq* (1988). This technique is believed to have the effect of oxidising the residual CO in the fuel to CO<sub>2</sub>, the reaction being catalysed by electrocatalyst sites present in the anode:



This technique provides fuel cell performance that is much closer to the performance

observed when no CO is present in the fuel stream. However, the air bleed technique does not usually improve the deleterious effects of CO<sub>2</sub> on performance and there are concerns over the long-term sustainability of the cell performance when this approach is employed. This is particularly the case if high levels of air bleed, equivalent to 4% and above of the total reformat fuel volume, are required.

However, the preferred technique for alleviating fuel cell performance reduction due to anode CO poisoning is to employ an anode electrocatalyst that is itself more poison-tolerant, but which still functions as a hydrogen oxidation catalyst in the presence of CO.

As described by, for example, Niedrach *et al* in *Electrochem. Technol.*, 5, 318, (1967), the use of a bimetallic anode electrocatalyst comprising platinum/ruthenium, rather than the more conventionally-used mono-metallic platinum-only electrocatalyst, shows a reduction in the poisoning effect of the CO at typical PEMFC operating temperatures. However, again, it was not possible fully to attain the performance observed on pure hydrogen, *ie* in the absence of CO in the fuel stream, by using this approach in isolation.

There have been a number of attempts to improve the performance of anode electrocatalysts operating in the presence of hydrogen fuels containing CO. These have taken the approach of modifying existing state-of-the-art catalysts, such as combining platinum/ruthenium with other components. In 1995, Chen *et al* (*J. Electrochem. Soc.*, 142, (10)) discussed the need to develop CO-tolerant catalysts and studied the oxidation of impure H<sub>2</sub> on Teflon<sup>®</sup>-bonded carbon-supported platinum/ruthenium/ tungsten oxide electrodes. The use of tungsten oxide (WO<sub>3</sub>) as a



promoter of improved activity of platinum catalysts towards impure  $H_2$  was not new. As far back as 1965, it was known that tungsten oxides were effective in promoting the electro-oxidation of CO on platinum-containing electrodes in acid-electrolyte fuel cells (Niedrach and Weinstock, *Electrochem. Technol.*, 3, 270-5 (1965)). A more recent  
5 example of a catalyst having improved CO tolerance is given in European patent specification no. EPA 838 872.

EPA 838 872 relates to a ternary catalyst comprising Pt-M-Y, wherein Pt-M is an alloy of platinum and one or more metals selected from the transition metal elements or from  
10 Groups IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press, and Y is a bronze forming element or an oxide thereof, characterised in that the Pt-M alloy is in intimate contact with Y, and provided that M is not Ru if Y is  $WO_3$ .

15 However, such electrocatalysts aimed at improving CO tolerance apparently do not also have the effect of improving performance when  $CO_2$  is present in the reformat fuel. Hence, for example, in the case of certain materials described in EPA 838 872, improved CO tolerance is observed, but at the same time the presence of  $CO_2$  in the reformat stream causes larger performance losses than those observed with state-of-  
20 the-art alloys of platinum and ruthenium. This behaviour is most likely due to the CO tolerance mechanism for the catalysts described in EPA 838 872 differing from that observed with Pt/Ru alloys.

We have now surprisingly found that significant improvement in both CO and  $CO_2$

tolerance can be achieved by providing an electrode structure in which the state-of-the-art Pt/Ru-type electrocatalyst is functionally linked with a further electrocatalyst. This has never before been achieved.

- 5 An anode structure of the present invention when used in a PEMFC shows improved tolerance to both CO and CO<sub>2</sub> poisons whilst maintaining high activity for the desired electrochemical reaction, and is therefore of use in fuel cells which use an impure feed. The anode structure may be of benefit in both phosphoric acid and solid polymer fuel cells. Specifically, it shows tolerance to both CO and CO<sub>2</sub> poisons in reformat fuel.
- 10 The anode structure may also be of benefit in these fuel cells when the fuel is methanol.

Accordingly, the present invention provides an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more

15 electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum.

- 20 The term "functionally linked" in the context of the present invention means that both materials are in ionic contact with each other. This may be achieved by adding an ion conducting material to each of the catalysts when they are formulated into the electrode structure of the invention. In the case of an anode structure for a PEMFC, the ion conducting material is a proton conducting material, which can be the same as that

employed as the polymeric electrolyte membrane of the MEA.

The Pt-M or Pt-X alloy is preferably more than a mere physical mixture of Pt with metal(s), since the platinum and metal(s) are preferably heat-treated to promote a measurable interaction between the platinum and metal(s) to change the intrinsic properties of the platinum metal. Heat-treatment causes a significant number of atoms of the metal(s) to be incorporated into the atomic crystal lattice, or unit cell, of the platinum particle. This process usually distorts the dimensions of the platinum unit cell, since the atoms of the metal(s) will generally be of a different size from those of the platinum, and this can usually be measured by techniques such as X-ray diffraction. The characteristic dimensions of the platinum unit cell, referred to by crystallographers as the lattice parameter, can be shown to have altered due to the fact that two or more metals, with different atomic sizes, have been incorporated into a single, homogeneous metal alloy particle at the atomic level.

Preferably, the one or more metals(s) X or M, when present, is or are selected from the groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press; for example, X metals can be from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, V, Ga, Zr, Hf and Sn; especially Ru, Mn, Ti, Co, Ni and Rh and M metals can be from the same group especially Ru and Rh.

Component Y may either be alloyed with the Pt-X alloy (the resulting alloy being as defined hereinbefore) or may be unalloyed but in physical contact with the alloy.

Component Y may be a bronze-forming element or an oxide thereof. A 'bronze' material is defined by Wold and Dwight in Solid State Chemistry - Synthesis, Structure, and Properties of Selected Oxides and Sulfides, Chapman & Hall as "... an oxide with intense colour (or black), having a metallic lustre and showing either semi-conducting or metallic behaviour. A principle characteristic of bronzes is their range of composition, which results in the transition metal exhibiting a variable formal valence." Suitable bronzes include non-stoichiometric alloys of the transition metal with hydrogen.

- 10 The component Y is suitably selected from one or more of the Group IVB to VIB elements and rhenium or an oxide thereof, for example Ti, V, Nb, Ta, Mo, W, Re, or an oxide thereof; suitably Ti, V, Ta, Mo, W, or an oxide thereof; preferably Mo or W, or an oxide thereof.
- 15 Preferably, the second catalytic component is one wherein the Pt-M is Pt (alone) or an alloy (as defined) of Pt/Ru.

The term "electrode structure" in the context of the present invention means the specific compositional aspects of those parts of the electrochemical cell at which the electrochemical reactions take place. It does not specifically refer to any particular physical embodiment of the invention. The physical embodiments of the invention can take several forms. The electrocatalyst materials can be applied to one side of a gas diffusion substrate material to produce an electrode, which can be either an anode or cathode, comprising the electrode structure of the invention.

Thus in a further aspect, the present invention provides an electrode comprising an electrode structure of the present invention wherein the electrocatalyst materials are present on one side of a gas diffusion substrate material.

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Alternatively the electrocatalyst materials can be applied to one side of the polymer electrolyte membrane material to produce a catalysed membrane, comprising the electrode structure of the invention.

10 Thus in a further aspect the present invention provides a catalysed membrane comprising an electrode structure according to the present invention wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material..

15 An MEA for use in, for example, a PEMFC, as herein described is a five layer unit, comprising a polymer electrolyte membrane in the centre, with an electrocatalyst containing layer either side of the membrane and a gas diffusion substrate layer in contact with the electrocatalyst containing layers on the opposite face of the layer to that in contact with the membrane. An MEA comprising the electrode structure of the  
20 invention, can be formed from electrodes as defined above, by bonding two electrodes, at least one of which comprises the electrode structure of the invention, either side of a polymer electrolyte membrane. Alternatively the MEA may be formed from the catalysed membrane by applying gas diffusion substrate materials either side of a

catalysed membrane, in which at least one catalysed side of the membrane comprises the electrode structure of the invention.

Thus in a further aspect, the present invention provides an MEA comprising an  
5 electrode structure according to the present invention.

In the above aspects of the present invention namely when formed into electrodes, catalysed membranes or an MEA from either of these two components, the two catalyst materials can be formulated into two separate layers which are applied to one side of  
10 either the gas diffusion substrate material or to the polymer electrolyte membrane, but in which they are still functionally linked. It is also possible that the two catalyst materials may be mixed together and formed into one layer containing both catalysts and applied to one side of either the gas diffusion substrate material or the polymer electrolyte membrane.

An electrode comprising the electrode structure of the invention may be formed wherein each catalyst is formulated into a separate layer in which a first layer comprising the first catalyst material, as herein defined, is in contact with one side of the gas diffusion substrate material, and a second layer comprising the second catalyst  
15 material is in contact with the opposite face of the first catalyst layer to that in contact with the gas diffusion substrate. Alternatively a catalysed membrane comprising the electrode structure of the invention may be formed wherein each catalyst is formulated into a separate layer in which a first layer comprising the second catalyst material, as herein defined, is in contact with one side of the polymer electrolyte membrane

material, and the second layer comprising the first catalyst material is in contact with the opposite face of the second catalyst layer to that in contact with the polymer electrolyte membrane.

5 In a further aspect, the present invention provides a fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which  
10 comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum.

In a final aspect, the present invention provides the use of an electrode structure according to the present invention in a fuel cell.

15 The invention will now be described further with reference to the following Examples and drawings in which:

**Figure 1:** shows fuel cell performance data of cell voltage vs time for operation  
20 of two PtRu (thick line and line with ●), PtRuW (line with ■), PtTiW (line with ×) and PtCoMo (line with ▲) catalysts in a gas stream containing 100ppm CO in hydrogen. The anode platinum loadings are respectively 0.37, 0.25, 0.29, 0.45 and 0.29 mg Pt/cm<sup>2</sup>.

**Figure 2** : shows fuel cell performance data of cell voltage vs time for operation of the two PtRu (thick line and line with ●), PtRuW (line with ■), PtTiW (line with ×) and PtCoMo (line with ▲) catalysts in a gas stream containing 25% CO<sub>2</sub> and 75% hydrogen. The anode platinum loadings are the same as in Figure 1.

**Figure 3** presents single cell performance data for electrode bilayers according to the invention operating in 25% CO<sub>2</sub> and 75% hydrogen. The bilayers comprise of catalyst layers of PtTiW (line with ×), PtRuW (line with ■), PtCoMo (line with ▲) and PtCoW (dashed line) containing 0.16, 0.12, 0.26 and 0.27 mg Pt cm<sup>-2</sup> and layers of PtRu catalyst at loadings of 0.13, 0.25, 0.14 and 0.24 mg Pt cm<sup>-2</sup>, respectively. Figure 3 also shows the comparative example PtRu (thick line) which is also presented in Figure 1.

**Figure 4** shows that, at the same time, the performance of the bilayer electrodes of the invention in hydrogen containing 100 ppm CO is significantly improved over the comparative PtRu sample performance decay, while the total platinum loading in both layers is very similar in all cases.

**Figure 5** shows the single cell performances of two MEA's, one an electrode bilayer according to the invention, and the other a single catalyst layer, operating on gas mixtures of CO and CO<sub>2</sub> in hydrogen, which has been used to simulate reformat gas compositions. The MEA's have been tested on two different gas mixtures; 40ppm CO and 25% CO<sub>2</sub> in hydrogen (closed symbols), and 100ppm CO and 25% CO<sub>2</sub> in hydrogen (open symbols). The bilayer



comprises of a catalyst layer of PtCoMo at loadings of 0.15 mg Pt/cm<sup>2</sup> and a layer of a PtRu catalyst at a loading of 0.31 mg Pt/cm<sup>2</sup> (lines with squares). The single layer electrode comprised of the same PtRu catalyst at a loading of 0.29 mg Pt/cm<sup>2</sup> (lines with circles).

5

### COMPARATIVE EXAMPLE 1

A catalyst containing platinum and ruthenium at 41.80 wt% Pt and 20.78wt% Ru supported on Cabot Vulcan XC72R carbon, was prepared using a process comprising the deposition of Pt onto the conductive carbon black substrate by the hydrolysis of an aqueous solution of chloroplatinic acid and ruthenium trichloride by a solution of sodium hydrogen carbonate in the presence of the carbon black, as disclosed in EP 450 849. The catalyst was reduced using aqueous formaldehyde solution, filtered, washed free of soluble chloride salts and dried at 100°C. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicating significant alloying of the Ru with the Pt. From this catalyst, a catalyst ink was prepared and a fuel cell anode was printed onto pre-TEFONATED Toray TPG90 paper. Inks and electrodes are prepared as detailed in Example 2 of European patent specification no. EPA 731 520. The platinum loading of this electrode was 0.37mgPt/cm<sup>2</sup>.

### COMPARATIVE EXAMPLE 2

A catalyst containing platinum and ruthenium at 19.2 wt% Pt and 9.3 wt% Ru

supported on Cabot Vulcan XC72R carbon, was prepared using the process as described in Comparative Example 1 and as disclosed in EP 450 849. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.88X, indicating significant alloying of the Ru with the Pt. An Electrode was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.25mgPt/cm<sup>2</sup>.

### COMPARATIVE EXAMPLE 3

A catalyst containing platinum, ruthenium and tungsten at 16.65wt%Pt, 8.32wt%Ru and 10.77wt% W was prepared. A PtRu catalyst (7.5g), as described in Comparative Example 2, was slurried in 1 litre of demineralised water for one hour. A 1 wt% solution of sodium tungstate in demineralised water was prepared containing 1.98g tungsten. This solution was converted to tungstic acid by passing it through an exchange column, comprising Dowex 50-X8 ion-exchange resin, and fed directly into the slurry. The resultant catalyst was stirred overnight and then filtered, dried at 105°C in air and fired at 500°C in a gas mixture containing 6%CO in CO<sub>2</sub>. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicating significant alloying of the Ru with the Pt, together with the presence of crystalline WO<sub>3</sub>. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.29mgPt/cm<sup>2</sup>.

## COMPARATIVE EXAMPLE 4

A catalyst containing Pt, Ti and W at 34.41 wt% Pt, 2.02wt% Ti and 10.63wt% W was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (16g) in a 6 litre solution of potassium hydrogen carbonate (25g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 8g Pt). The resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was dried at 100°C in air. The catalyst was re-slurried in a litre solution of potassium hydrogen carbonate (2.5g) and heated till under reflux. A 2wt% solution of titanium trichloride (containing 0.45g Ti) and urea (3.39g) was added dropwise. The ratio of alkali to metal salts for both steps was such as to ensure complete hydrolysis and precipitation of the metal hydrous oxides/hydroxides onto the carbon.

The slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The wet cake was then dispersed in a litre of demineralised water. To this slurry was added dropwise a 1wt% solution of tungsten (2.32g) in water. This was prepared by the dissolution of tungsten powder in hydrogen peroxide solution, followed by decomposition of the excess peroxide by platinum black. The combined slurry was then evaporated to dryness. The resulting catalyst was then heated at 650°C in flowing 5% hydrogen in nitrogen for 1 hour. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.93X, which indicated little alloying of the components. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.45mgPt/cm<sup>2</sup>.

## COMPARATIVE EXAMPLE 5

A catalyst containing Pt, Co and Mo at 21.0wt% Pt, 0.2wt% Co and 1.0wt% Mo was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (94.5g) in a 6 litre solution of sodium hydrogen carbonate (67.4g) under reflux, was added first a 2wt% solution of chloroplatinic acid (containing 24.2g Pt), followed by a 2wt% solution of cobalt dichloride (containing 1.7g Co). The amount of sodium hydrogen carbonate was calculated to be sufficient to just precipitate both Pt and Co as their hydrous oxides/hydroxides. The resulting catalyst was filtered, washed with demineralised H<sub>2</sub>O until chloride free and dried at 100°C. A portion of the dried catalyst (21.8g) was reslurried in 1.5 litres of demineralised H<sub>2</sub>O and stirred. To this was added disodium molybdate dihydrate (1.7g) and the slurry stirred until complete dissolution. To the resulting slurry was added a solution of 1,8-hydroxyquinoline (1.0g) in 40 cm<sup>3</sup> of ethanol. The amount of 1,8-hydroxyquinoline added being 2 molar equivalents of the amount of Mo added. The slurry was heated until under reflux and the pH adjusted to 4 by the addition of acetic acid. The slurry was boiled for 60 minutes to remove the ethanol, after which the slurry was cooled, filtered, washed free of salts and dried at 100°C. The dried catalyst was heat treated under flowing 10%H<sub>2</sub>/N<sub>2</sub> for 1 hour at 650°C to decompose the 1,8-hydroxyquinoline. X-ray diffraction of resulting catalyst showed a single cubic phase with a lattice parameter of 3.91, which indicates little alloying of the components. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1. The platinum loading of this electrode was 0.29mgPt/cm<sup>2</sup>.

### COMPARATIVE EXAMPLE 6

A catalyst containing Pt and Ru at 38.7 wt%Pt and 20.7 wt%Ru supported on Cabot Vulcan XC72R carbon was prepared as described in Comparative Example 1. X-ray analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.90X, indicating significant alloying of the Ru with the Pt. An electrode containing this catalyst at a platinum loading of 0.29mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1.

### EXAMPLE 1 - (Pt/Mo/Co)/(Pt/Ru)

A catalyst containing Pt, Mo and Co at 20.30 wt%Pt, 1.44wt%Co and 0.65wt%Mo was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (30.2g) in a solution of sodium hydrogen carbonate (22.3g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 8g Pt) and cobalt dichloride (containing 0.6g Co). After refluxing for 2.5 hrs, the resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was dried at 100°C in air.

The dried catalyst was then re-dispersed in 1 litre of demineralised water for one hour at ambient temperature. To this slurry was added a solution of molybdenum (1.21g) prepared by passing a 1wt% solution of sodium molybdate through an ion exchange column containing Dowex 50-X8 ion exchange resin to convert to colloidal molybdic acid. The combined slurry was then evaporated to dryness. The resulting catalyst was

then heated at 695°C in flowing 5% hydrogen in nitrogen to ensure reduction and alloying of the components. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.87X, indicating significant alloying of the components

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An electrode containing the catalyst at a platinum loading of 0.26mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.14mgPt/cm<sup>2</sup>.

10

#### EXAMPLE 2 - (Pt/W/Co)/(Pt/Ru)

A catalyst containing Pt, W and Co at 14.7wt%Pt, 1.0wt%Co and 3.8wt% W was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon (32g) in 6 litres of a solution of sodium hydrogen carbonate (18.5g) under reflux, was added a 2wt% solution of chloroplatinic acid (containing 5.7g Pt). The resulting slurry was heated under reflux for 2 hrs, before being filtered and washed with demineralised water, until no chloride was detected in the washings. The catalyst was then dried at 100°C in air.

The dried catalyst was re-dispersed in 6 litres of sodium hydrogen carbonate (1.1g) solution and heated till under reflux. To this slurry was added a 2wt% solution of cobalt dichloride (containing 0.4g Co). The slurry was then filtered and washed with demineralised water until no chloride was detected in the washings. The wet cake was re-slurried in 1 litre of demineralised water for 1 hr at ambient temperature. To this was

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added was added a solution of tungsten (1.5g). The tungsten solution was prepared by dissolving tungsten powder in hydrogen peroxide (100 cm<sup>3</sup> of 28wt% H<sub>2</sub>O<sub>2</sub> solution), followed by decomposition of the excess peroxide by platinum black, and subsequent dilution to a 1wt% solution by demineralised water. The combined slurry was then evaporated to dryness. The resulting catalyst was then heated to 900°C in flowing nitrogen for 1 hour. X-ray diffraction analysis of the resulting catalyst showed a single cubic phase with a lattice parameter of 3.90X indicating significant alloying of the components.

10 An electrode containing this catalyst at a platinum loading of 0.27mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of a catalyst containing Pt and Ru at 37.1 wt%Pt and 17.9 wt%Ru supported on Cabot Vulcan XC72R carbon was prepared as described in Comparative Example 1, was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.24 mgPt/cm<sup>2</sup>. X-ray analysis of this catalyst showed a single cubic phase with a lattice parameter of 3.90X, indicating significant alloying of the Ru with the Pt. An electrode containing this catalyst at a platinum loading of 0.29mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1.

### EXAMPLE 3 - (Pt/Ru/W)/(Pt/Ru)

A catalyst containing Pt, Ru and W was prepared as described in Comparative Example 2. An electrode containing this catalyst at a platinum loading of 0.12mgPt/cm<sup>2</sup> was

prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst as used in Example 2 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.25mgPt/cm<sup>2</sup>.

5

#### EXAMPLE 4 - (Pt/Ti/W)/(Pt/Ru)

A catalyst containing Pt, Ti and W was prepared as described in Comparative Example

4. An electrode containing this catalyst at a platinum loading of 0.16mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 2 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.13mgPt/cm<sup>2</sup>.

15

#### EXAMPLE 5 - (PtMoCo)/(PtRu)

A catalyst containing Pt, Co and Mo was prepared as described in Comparative Example 5. An electrode containing this catalyst at a platinum loading of 0.15mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 6 was applied using the method described in Comparative Example 1. The addition loading in this catalyst layer was 0.31 mgPtc<sup>2</sup>.

20



TABLE 1

Example Number	Catalyst	Assay Characterisation Data /wt% of total catalyst weight			Atomic Ratio	XRD Characterisation	
		Pt	2 <sup>nd</sup> Metal	3 <sup>rd</sup> Metal		Crystallite Size /nm	Pt lattice parameter /Å
Comp. 1	PtRu	41.80	20.78		51:49	2.6	3.87
Comp. 2	PtRu	19.2	9.3		52:48	1.9	3.88
Comp. 3	PtRuW	16.65	8.32	10.77	38:36:26	4.6	3.87
Comp. 4	PtTiW	34.41	2.02	10.63	64:15:21	5.6	3.93
Comp. 5	PtCoMo	21.9	0.2	1.0	89:03:08	4.5	3.91
Comp. 6	PtRu	38.7	20.7		49:51	2.7	3.90
1	PtCoMo	20.30	1.44	0.65	77:18:05	4.2	3.87
	PtRu	41.80	20.78		51:49	2.6	3.87
2	PtCoW	14.7	1.0	3.76	67:15:18	3.1	3.90
	PtRu	19.2	9.3		52:48	1.9	3.88
3	PtRuW	16.65	8.32	10.77	38:36:26	4.6	3.87
	PtRu	37.06	17.89		52:48	3.2	3.90
4	PtTiW	34.41	2.02	10.63	64:15:21	5.6	3.93
	PtRu	19.2	9.3		52:48	1.9	3.88
5	PtCoMo	21.9	0.2	1.0	89:03:08	4.5	3.91
	PtRu	38.7	20.7		49:51	2.7	3.90

## EXAMPLE 6-PREPARATION OF MEAs

- 5 The electrode structures of the invention were first produced as anodes and then bonded to membranes to form MEAs. as described in Example 2 of EP 731 520. The MEA was

fabricated by hot-pressing the anode and a pure platinum catalyst cathode (with a platinum loading of  $0.6\text{mg Pt/cm}^2$ ) against each face of a solid proton-conducting electrolyte membrane. The membrane used was the perfluorinated membrane Nafion® 115 (from Du Pont de Nemours). MEAs of  $6.5\text{ cm}^2$  area were formed by hot-pressing at pressures of 100 psi ( $1\text{ psi} = 6.89 \times 10^3\text{ N/m}^2$ ) over the MEA, at temperatures exceeding the glass transition temperature of the membrane, as is commonly practised in the art. MEAs of  $240\text{ cm}^2$  area were formed by hot pressing at pressures of 400 psi over the MEA.

#### EXAMPLE 7-PERFORMANCE EVALUATION

The MEAs were evaluated in a PEMFC single cell. The single cell consists of graphite plates into which flowfields are machined to distribute the reactant gases, humidification water and heating and cooling water and to remove products. The MEA was located between the appropriate flowfield plates. The cell is compressed, typically to a gauge pressure of 70 psig above the reactant gas pressure.

The "fuel cell performance" was assessed by measuring the voltage at a fixed current density of  $500\text{ mA cm}^{-2}$ . The fuel cell operated under conditions representative of those employed in practical PEM fuel cells. These conditions were typically a reactant gas inlet temperature of  $80^\circ\text{C}$ , a pressure of both hydrogen and air reactants of 3 atmospheres. For  $6.45\text{ cm}^2$  MEAs, the reactant gas streams were kept constant at 0.1SLPM (standard litres at 1 bar and  $0^\circ\text{C}$  per minute); 0.125 SLPM for 25%  $\text{CO}_2$  and 75% hydrogen; and 0.4 SLPM for oxygen. For  $240\text{ cm}^2$  MEAs, the fuel to air gas stoichiometry was 1.5/2. For the single cell reformat tolerance experiments, the anode

gas stream was changed at time  $t=0$  from pure hydrogen to gas streams composed of 100ppm CO in hydrogen, 25% CO<sub>2</sub> in hydrogen, 40ppm CO and 25% CO<sub>2</sub> in hydrogen or 100ppm CO and 25% CO<sub>2</sub> in hydrogen. The fuel cell performance using the binary gas mixtures was performed using the 6.45 cm<sup>2</sup> MEAs, while testing using the ternary gas mixtures was performed using the 240 cm<sup>2</sup> MEAs. At constant current density of 0.5 Acm<sup>-2</sup>, the cell potential was then monitored with time in order to assess the CO and the CO<sub>2</sub> tolerance of different catalysts under practical conditions. Table 2 summarises the CO, CO<sub>2</sub> and CO/CO<sub>2</sub> tolerances of the catalysts described in the Examples in the form of voltage losses (in mV) on the different poisoning gas streams, when compared to operation on pure hydrogen. The lower the voltage loss, the more resistant the catalyst or catalyst combination is towards being poisoned on that particular gas stream.

Figure 1 shows fuel cell performance data of cell voltage vs time for operation of two PtRu, PtRuW, PtTiW and PtCoMo catalysts in a gas stream containing 100ppm CO in hydrogen. The anode platinum loadings are respectively 0.37, 0.25, 0.29, 0.45 and 0.29 mg Pt/cm<sup>2</sup>. Figure 1 shows that the single cell voltages for all five MEAs decay from their value at  $t=0$  min when the cell is operated with pure hydrogen. Figure 1 shows that the performance curves of the two MEAs containing PtRu anode catalysts, one labelled "standard" PtRu and the other labelled "advanced" PtRu. This represents the range of CO tolerance performance found with state of the art PtRu catalysts as a function of Pt loading on the carbon and Pt loading in the catalyst layer. The MEA containing the advanced PtRu catalyst, shows the lowest drop in performance on switching between pure hydrogen and 100ppm CO in hydrogen. This catalyst has a higher Pt loading on carbon and a higher loading of catalyst in the electrode compared to the standard PtRu

catalyst. The electrode containing the advanced PtRu catalyst would be expected to give a higher performance due to the higher density of Pt in the catalyst layer. The performance curves of the MEA's containing the three ternary catalysts, PtRuW, PtTiW and PtCoMo on 100ppm CO in hydrogen show them lying between the two PtRu performance curves, indicating comparable CO tolerance. Considering that the dispersion of the catalyst particles as shown in Table 1 as Pt crystallite size, are significantly inferior to those displayed by the two PtRu catalysts, then these catalysts are intrinsically more CO tolerant than state of the art PtRu catalysts, in terms of specific activity (ie activity per actual surface area of Pt present).

Figure 2 shows fuel cell performance data of cell voltage vs time for operation of the two PtRu, PtRuW, PtTiW and PtCoMo catalysts in a gas stream containing 25% CO<sub>2</sub> and 75% hydrogen. The anode platinum loadings are the same as in Figure 1. Figure 2 shows that the single cell voltages for all five MEAs decay from their value at t=0 min when the cell is operated with pure hydrogen. The performances of the electrodes containing the PtRu catalysts degrades by 19 and 38 mV respectively, on the introduction of the gas mixture containing 25% CO<sub>2</sub> and 75% hydrogen. In contrast, the performance of the electrodes containing the three ternary catalysts degrade by larger amounts, with the PtCoMo catalyst losing 211 mV on introduction of the CO<sub>2</sub>/H<sub>2</sub> gas mixture. This shows that although the ternary catalysts have good CO tolerance, they have inferior CO<sub>2</sub> tolerance to the 'state-of-the-art' PtRu catalysts.

Figure 3 presents single cell performance data for electrode bilayers according to the invention operating in 25% CO<sub>2</sub> and 75% hydrogen. The bilayers comprise of catalyst

layers of PtTiW, PtRuW, PtCoMo and PtCoW containing 0.16, 0.12, 0.26 and 0.27 mg Pt cm<sup>-2</sup> and layers of PtRu catalyst at loadings of 0.13, 0.25, 0.14 and 0.24 mg Pt cm<sup>-2</sup>, respectively. Figure 3 also shows the comparative example PtRu which is also presented in Figure 1. The bilayer electrodes according to the invention show small  
5 decays when the gas stream is changed at t=0 min from pure hydrogen to 25%CO<sub>2</sub> and 75% hydrogen. The performance decay of the PtRuW catalyst when as a bilayer with PtRu shows a significant reduction. The other electrode samples exhibit a decay around 25 mV, very close to the comparative PtRu electrode. Therefore, the combination of Pt ternary catalysts with PtRu catalysts, has overcome the CO<sub>2</sub> "in-tolerance" of these  
10 catalyst seen, when tested as single catalyst layers.

Figure 4 shows that, at the same time, the performance of the bilayer electrodes of the invention in hydrogen containing 100 ppm CO is significantly improved over the comparative PtRu sample. When at t=0 min the gas stream is changed from pure  
15 hydrogen to hydrogen containing 100 ppm CO, all samples exhibit, after some induction time, a decay of the single cell voltage. This decay is 166 mV for the comparative PtRu sample. All bilayer samples show lower performance decay, while the total platinum loading in both layers is very similar in all cases. The PtCoMo/PtRu bilayer electrode of the invention shows a performance decay as low as approximately  
20 88 mV. In addition, the PtCoW/PtRu bilayer electrode of the invention shows a performance decay of 73 mV, although with a higher overall electrode loading of 0.51 mg Pt/cm<sup>2</sup>.

Figure 5 shows the single cell performances of two MEA's, one an electrode bilayer

according to the invention, and the other a single catalyst layer, operating on gas mixtures of CO and CO<sub>2</sub> in hydrogen, which has been used to simulate reformat gas compositions. The MEA's have been tested on two different gas mixtures; 40ppm CO and 25% CO<sub>2</sub> in hydrogen, and 100ppm CO and 25% CO<sub>2</sub> in hydrogen. The bilayer comprises of a catalyst layer of PtCoMo at loadings of 0.15 mg Pt/cm<sup>2</sup> and a layer of a PtRu catalyst at a loading of 0.31 mg Pt/cm<sup>2</sup>. The single layer electrode comprised of the same PtRu catalyst at a loading of 0.29 mg Pt/cm<sup>2</sup>. Figure 5 shows that the performance of the bilayer electrode is superior to the single layer with both the gas mixtures tested. In particular, the differences between the two electrodes is increased with the gas mixture with 100ppm CO.

Clearly, the bilayer electrode according to the invention shows improved performance when tested in gas streams of CO in hydrogen, CO<sub>2</sub> in hydrogen and mixtures of CO and CO<sub>2</sub> in hydrogen, when compared to single layer electrodes of similar Pt loading. In particular, the combination of two different catalysts within the bilayer electrode have shown unexpectedly improved performances based on their performances as single layers.

TABLE 2

Example	Catalyst(s)	Pt loading /mgPtcm <sup>-2</sup>	Voltage Losses on Different Poisoning Gas Streams			
			/mV			
			100ppmCO /H <sub>2</sub>	25%CO <sub>2</sub> /H <sub>2</sub>	40ppmCO/ 25%CO <sub>2</sub> /H <sub>2</sub>	100ppmCO/ 25%CO <sub>2</sub> /H <sub>2</sub>
Comp. 1	PtRu	0.37	166	19	-	-
Comp. 2	PtRu	0.25	325	38	-	-

Comp. 3	PtRuW	0.29	177	56	-	-
Comp. 4	PtTiW	0.45	195	51	-	-
Comp. 5	PtCoMo	0.29	274	211	-	-
Comp. 6	PtRu	0.29	-	-	114	173
1	PtCoMo/PtRu	0.26/0.14	88	29	-	-
2	PtCoW/PtRu	0.27/0.24	73	22	-	-
3	PtRuW/PtRu	0.12/0.25	110	44	-	-
4	PtTiW/PtRu	0.16/0.13	165	29	-	-
5	PtCoMo/PtRu	0.15/0.31	-	-	61	83

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531 Rec'd TC

09/857759

08 JUN 2001

1. An electrode structure comprising a first catalytic component and a second catalytic component, wherein:
  - (a) said first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y, wherein Y is Mo, W or an oxide of Mo or W, and optionally a third metal component X which is alloyed with the platinum and which is one or metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; and
  - (b) said second catalytic component comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the platinum and is one or more metals selected from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; andwherein the first and second catalytic components are in ionic contact with each other.
2. An electrode structure according to claim 1 wherein X is selected from Ru, Mn, Co, Ni, Rh and Ni.
3. An electrode structure according to claim 1 or claim 2, wherein M is selected from Ru or Rh.
4. An electrode structure according to claim 1, wherein the first catalytic component is selected from: Pt/Mo, Pt/Mo/Co, Pt/W/Co, Pt/Ru/WO<sub>3</sub> and Pt/Ti/W; and the second catalytic component is Pt/Ru.



5. An electrode comprising an electrode structure according to any preceding claim wherein the electrocatalyst materials are present on one side of a gas diffusion material.
6. A catalysed membrane comprising an electrode structure according to any one or more of claims 1 to 4 wherein the electrocatalyst materials are present on one side of the polymer electrolyte membrane material.
7. An MEA comprising an electrode structure according to any one or more of claims 1 to 4.
8. An electrode according to claim 5, a catalysed membrane according to claim 6 or an MEA according to claim 7 wherein the two catalyst materials are formulated into two separate layers.
9. An electrode according to claim 5, a catalysed membrane according to claim 6 or an MEA according to claim 7 wherein the two catalyst materials are formulated into one mixed layer.
10. A fuel cell an electrode structure, comprising a first catalytic component and a second catalytic component, characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula Pt-Y where Y is a bronze forming element, and optionally a third metal component X which is alloyed with the platinum, and the second catalytic component which comprises one or more electrocatalyst(s) of formula Pt-M, where M is a metal alloyed with the

platinum.

11. Use of an electrode structure according to any one or more of claims 1 to 8 in a fuel cell.
16. An electrode, such as an anode, such as a fuel cell anode; an electrochemical device, such as an MEA; a use; or a method, substantially as hereinbefore described with particular reference to the examples.

FIGURE 1

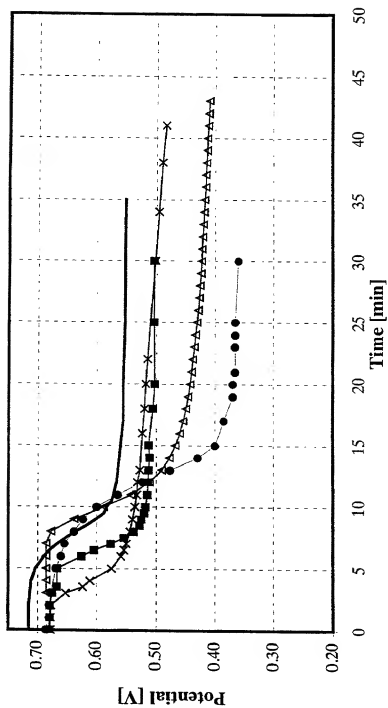


FIGURE 2

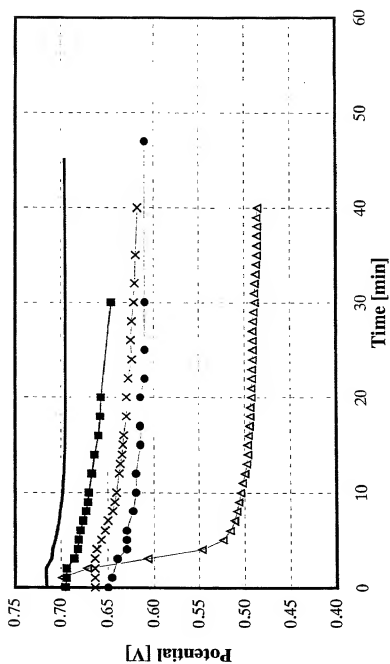


FIGURE 3

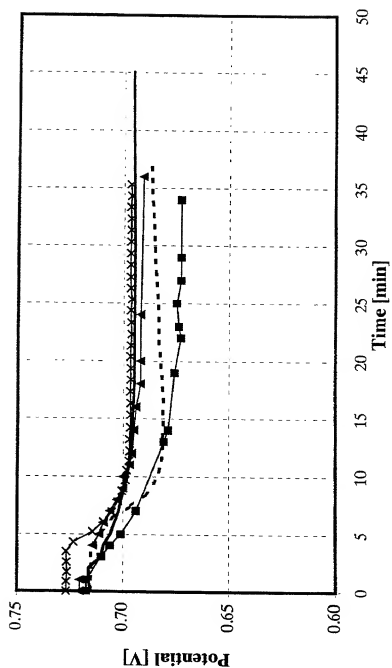


FIGURE 4

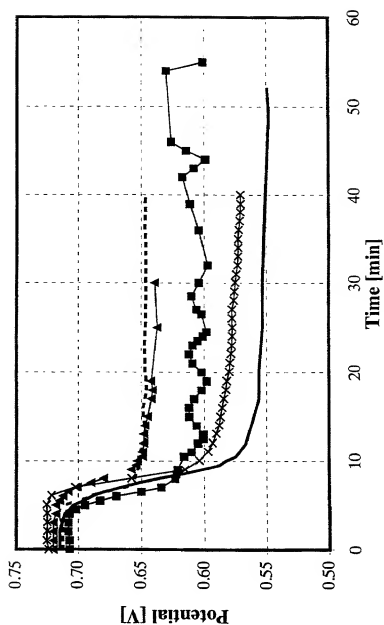
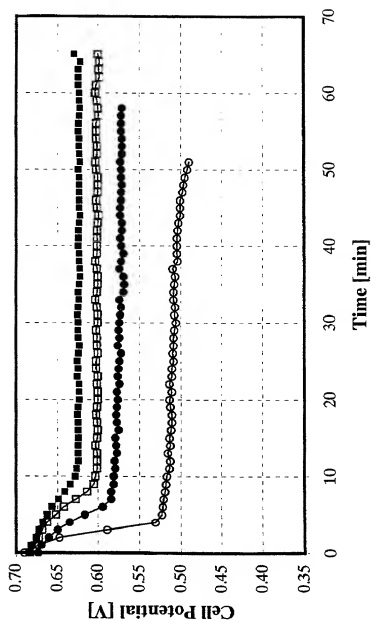


FIGURE 5



# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

ELECTRODE STRUCTURE,

the specification of which is attached hereto unless the following box is checked:



was filed on June 8, 2001 as

United States Application Number or PCT International Application Number 09/857,759

and was amended on June 8, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Not Claimed

9826940.0

Great Britain

December 9, 1998

(Number)

(Country)

(Day/Month/Year Filed)



(Number)

(Country)

(Day/Month/Year Filed)



I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:



(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

(Application Number)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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